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Formation of Alkylsilane-Based Monolayers on Gold

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A team of chemists from the University of Michigan in Ann Arbor have made a surprising discovery: At room temperature, the chemical reaction of compounds with silicon-hydrogen bonds with gold surfaces yields a new class of alkylsilane($\text{CH}_3(\text{CH}_2)_n\text{Si}$)-based monolayers. The monolayers are reminiscent of the self-assembled monolayers (SAMs) formed by alkanethiols ($\text{CH}_3(\text{CH}_2)_n\text{SH}$). However, they exhibit a different chemical behavior that may prove advantageous in microelectronics and micro-contact printing. The alkylsilane monolayers have been characterized using soft X-ray photoelectron spectroscopy (SXPS) and reflection absorption infrared spectroscopy (RAIRS).

The physical properties of metal surfaces can be modified through the adsorption of small molecules. For example, hydrocarbons modified with carboxylic acid (RCOOH) or thiol (RSH) functional groups have been particularly well studied. In recent years, scientists have shown that the adsorption of alkanethiols ($\text{CH}_3(\text{CH}_2)_n\text{SH}$) on gold surfaces may have many applications, including molecular electronics and micro-contact printing. But these applications have met some limitations due to surface defects introduced by the adsorption process and to degradation caused by atmospheric ozone. We have explored the use of alkylsilanes ($\text{CH}_3(\text{CH}_2)_n\text{SiH}_3$) as a replacement for the thiol groups.

We synthesized monolayers of hexylsilane ($\text{C}_6\text{H}_{13}\text{SiH}_3$), octylsilane ($\text{C}_8\text{H}_{17}\text{SiH}_3$), and octadecylsilane ($\text{C}_{18}\text{H}_{37}\text{SiH}_3$) by exposing gold surfaces to one of the alkylsilanes (**Figure 1**) in an ultrahigh vacuum (UHV) chamber. The gold-alkylsilane samples have been characterized in UHV by reflection absorption infrared spectroscopy (RAIRS) at the University of

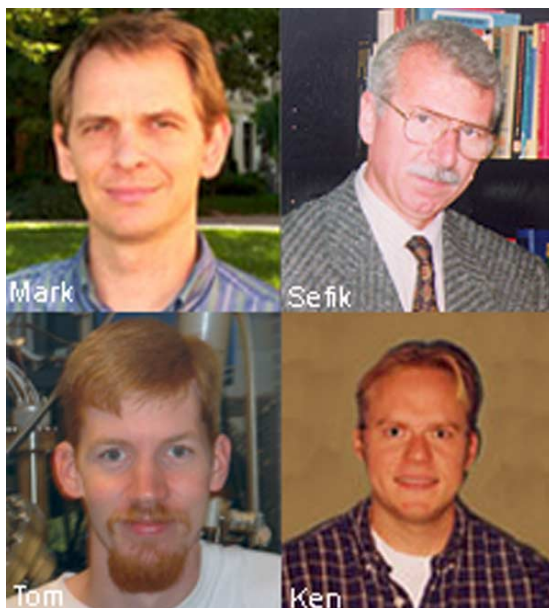
Michigan in Ann Arbor, and soft x-ray photoelectron spectroscopy (SXPS) at beamline U8B at the NSLS.

The silicon 2p core levels were measured to have a binding energy of -99.8 electronvolts (eV), as shown in figure 2A, suggesting that silicon is bound to the gold surface and that no silicon-hydrogen bonds remain. We measured a full width

at half-maximum of 0.4 eV, which is smaller than that observed for bulk, crystalline silicon using the same beamline and monochromator, thus indicating that silicon atoms are in a chemically homogeneous environment.

The valence band spectra of the alkylsilane-based monolayers (**Figure 2**) bear a striking resemblance to valence band data of frozen alkanes ($\text{C}_n\text{H}_{2n+2}$) of the same length, indicating that the hexyl, octyl, and octadecyl chains have remained intact.

We have not observed a silicon-hydrogen stretch in the RAIRS spectra for alkylsilane monolayers on gold (**Figure 3**). The silicon-hydrogen stretch at 2150 cm^{-1} is the most intense feature observed for liquid alkylsilane (**Figure 3D**). The absence of this feature in the monolayers suggests that no silicon-hydrogen bonds remain after chemical adsorption. The observed carbon-hydrogen stretching modes between 2850 and 3000 cm^{-1} , are consistent with the alkyl ($\text{C}_n\text{H}_{2n+1}$) chains being angled away from the surface.



Clockwise from top left: Mark Banaszak Holl, Sefik Sözer, Ken Nicholson, and Tom Owens (lead author).

The combination of SXPS and RAIRS data suggests that when the alkylsilane monolayers bind to the gold surface, all three silicon-hydrogen bonds react with the gold surface and silicon forms bonds to three surface gold atoms, which is unlike single gold-sulfur bonds in structures made of thiol bound to gold.

Also, the alkanethiol and alkylsilane layers exhibit different oxidation behaviors. Oxidation of sulfur atoms causes alkanethiol monolayers to fall apart, while oxidation of the alkylsilane layers knits the silicon atoms together by forming a siloxane network and maintaining the integrity of the alkyl chains and the surface monolayer.

The unique properties of the alkylsilane layers may lend them to applications requiring durable layers and may provide an interesting route for the formation of patterned structures.

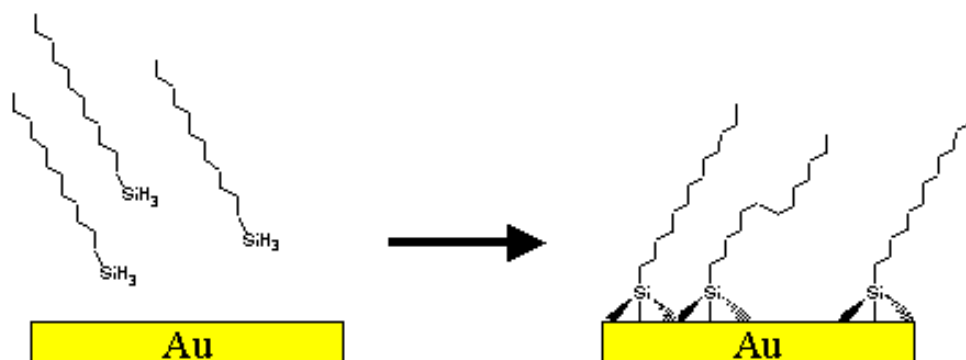


Figure 1. Schematic representation of alkylsilane ($\text{CH}_3(\text{CH}_2)_n\text{Si}$) bonding to gold surface.

Figure 2. X-ray photoemission spectra (photon energy = 160 eV) of (1) octadecylsilane, (2) octylsilane, and (3) hexylsilane monolayers on (4) gold. (A) Silicon 2p and gold 4f core levels, and (B) valence band.

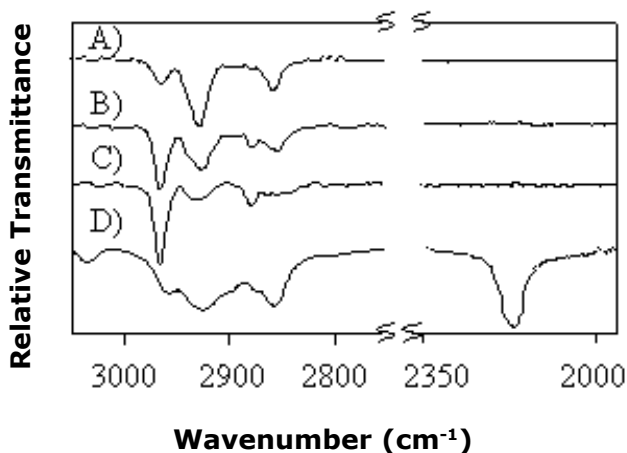
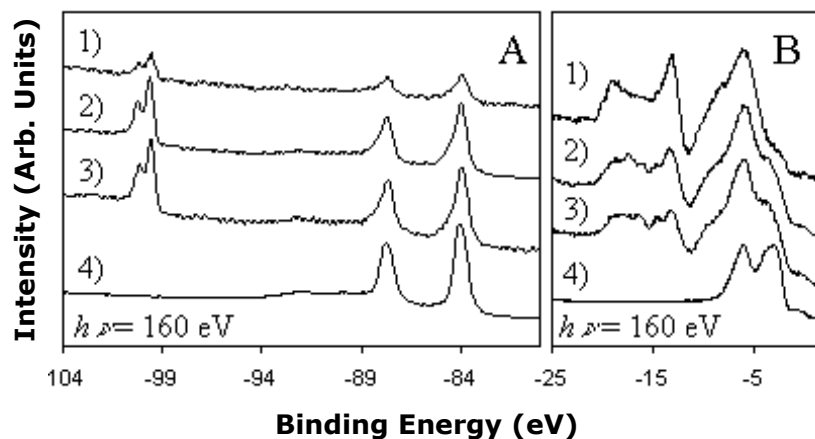


Figure 3. Reflection-absorption infrared spectroscopy (RAIRS) spectra ($3050\text{--}2750$ and $2350\text{--}2000\text{ cm}^{-1}$) for monolayers of (A) octadecylsilane, (B) octylsilane, and (C) hexylsilane on gold. A solution infrared spectrum of octylsilane (D) is included for comparison.